

## REPORT DOCUMENT



|  |  |  |  |  |  |  |  |           |                    |                         |  |  |  |  |  |
|--|--|--|--|--|--|--|--|-----------|--------------------|-------------------------|--|--|--|--|--|
| 1a. REPORT SECURITY CLASSIFICATION: <b>Unclassified</b> MAY 21 1991  |  |  |  | 3. DISTRIBUTION/AVAILABILITY OF REPORT<br><br>Distribution unlimited                           |  |  |  |           |                    |                         |  |  |  |  |  |
| 2a. SECURITY CLASSIFICATION AUTHORITY  |  |  |  | 5. MONITORING ORGANIZATION REPORT NUMBER(S)  |  |  |  |           |                    |                         |  |  |  |  |  |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE  |  |  |  | 7a. NAME OF MONITORING ORGANIZATION<br><br>Office of Naval Research                            |  |  |  |           |                    |                         |  |  |  |  |  |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br><br>Technical Report #1   |  |  |  | 7b. ADDRESS (City, State, and ZIP Code)<br>800 North Quincy Street<br>Arlington, VA 22217-5000 |  |  |  |           |                    |                         |  |  |  |  |  |
| 6a. NAME OF PERFORMING ORGANIZATION<br><br>Cornell University  |  | 6b. OFFICE SYMBOL<br>(If applicable)   |  | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER  |  |  |  |           |                    |                         |  |  |  |  |  |
| 8a. NAME OF FUNDING / SPONSORING ORGANIZATION<br><br>Office of Naval Research  |  | 8b. OFFICE SYMBOL<br>(If applicable)   |  | 10. SOURCE OF FUNDING NUMBERS  |  |  |  |           |                    |                         |  |  |  |  |  |
| 6c. ADDRESS (City, State, and ZIP Code)<br>Department of Chemistry<br>Baker Laboratory, Ithaca, NY 14853-1301  |  | 8c. ADDRESS (City, State, and ZIP Code)<br>800 North Quincy Street<br>Arlington, VA 22217-5000 |  | PROGRAM ELEMENT NO.  |  | PROJECT NO.  |  | TASK NO.  |                    | WORK UNIT ACCESSION NO. |  |  |  |  |  |
| 11. TITLE (Include Security Classification)<br>Photogenerated Amines and Diamines: Novel Curing Systems for Thin Film Coatings.  |  |  |  |  |  |  |  |           |                    |                         |  |  |  |  |  |
| 12. PERSONAL AUTHOR(S)<br>Jean M.J. Fréchet and James F. Cameron   |  |  |  |  |  |  |  |           |                    |                         |  |  |  |  |  |
| 13a. TYPE OF REPORT<br>Technical   |  |  | 13b. TIME COVERED<br>FROM _____ TO _____ |  |  | 14. DATE OF REPORT (Year, Month, Day)<br>5-1-91      |  |           | 15. PAGE COUNT     |                         |  |  |  |  |  |
| 16. SUPPLEMENTARY NOTATION<br><br>ACS Polymeric Materials Science and Engineering Volume 64 (1991)   |  |  |  |  |  |  |  |           |                    |                         |  |  |  |  |  |
| 17. COSATI CODES   |  |  |  | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)              |  |  |  |           |                    |                         |  |  |  |  |  |
| FIELD  |  |  |  | GROUP  |  |  |  | SUB-GROUP |                    |                         |  |  |  |  |  |
|  |  |  |  |  |  |  |  |           |                    |                         |  |  |  |  |  |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br><br>The photogeneration of organic amines from $\alpha,\alpha$ -dimethyl-3,5-dimethoxybenzyl carbamates is described. The photoactive carbamates are prepared easily through reactions involving the Li catalyzed addition of isocyanates to $\alpha,\alpha$ -dimethyl-3,5-dimethoxybenzyl alcohol or through the use of active ester chemistry. A variety of active carbamates that can be used to generate primary or secondary amines as well as diamines has been tested successfully. Free amines are liberated upon exposure of the carbamates to UV radiation below 300 nm. Preliminary tests indicate that photoactive carbamates incorporating o-nitrobenzyl groups are also readily obtainable from isocyanates. |  |  |  |  |  |  |  |           |                    |                         |  |  |  |  |  |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT<br><input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS  |  |  |  |  |  | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unclassified |  |           |                    |                         |  |  |  |  |  |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>Dr. K. J. Wynne   |  |  |  |  |  | 22b. TELEPHONE (Include Area Code)<br>(202) 696-4410 |  |           | 22c. OFFICE SYMBOL |                         |  |  |  |  |  |

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-91-J-1338

R&T Code 413t003

Technical Report No. 1

Photogenerated Amines and Diamines:  
Novel Curing Systems for Thin Film Coatings

by

Jean M.J. Fréchet and James F. Cameron

Prepared for Publication

in the

ACS Polymeric Materials Science and  
Engineering Volume 64 (1991)

Cornell University

Department of Chemistry

Baker Laboratory

Ithaca, NY 14853-1301



DTIC  
COPY  
INSPECTED  
6

|              |         |
|--------------|---------|
| By           |         |
| Distribution |         |
| Availability |         |
| Dist         | Special |
| A-1          |         |

Reproduction in whole or in part is permitted for any purpose  
of the United States Government

This document has been approved for public release and  
sale; its distribution is unlimited.

91 5 20 008

91-00161



# PHOTOGENERATED AMINES AND DIAMINES: NOVEL CURING SYSTEMS FOR THIN FILM COATINGS

Jean M. J. Fréchet and James F. Cameron

Department of Chemistry, Baker Laboratory  
Cornell University, Ithaca, NY 14850-1301 USA

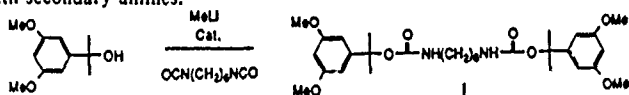
The photogeneration of acid within solid matrices such as thin films or coatings has led to significant developments in the areas of photocurable coatings [1], imaging materials [2], and resists for microlithography [3]. In these systems, the ability to photogenerate acid *in situ* within a solid matrix is key to subsequent steps that may involve polymerization [1], depolymerization [4], catalyzed thermolysis [3] or electrophilic aromatic substitution processes [5].

In view of the wealth of chemistry that may be promoted or catalyzed by base and is therefore applicable to coating, imaging, and resist chemistry, it is desirable to prepare efficient organic photo-precursors of amines that may be used efficiently in the solid state.

We have developed recently [6] a family of carbamates based on  $\alpha,\alpha$ -dimethyl-3,5-dimethoxybenzyl (Ddz) chemistry that can be used to generate amines by exposure to UV light below 300nm. This report describes some of these carbamates as well as another family of active compounds that may also be used with longer wavelength radiation and possess extremely high quantum efficiencies in the solid state.

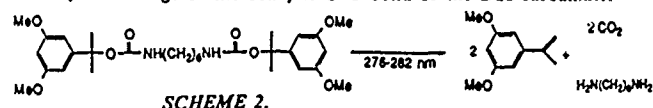
## 1. Chemistry of $\alpha,\alpha$ -dimethyl-3,5-dimethoxybenzyl carbamates.

The procedure used for the preparation of  $\alpha,\alpha$ -dimethyl-3,5-dimethoxybenzyl (Ddz) carbamates are described elsewhere [6]. Typically the most convenient route for the Ddz protection of primary amines or diamines involves the reaction of the corresponding isocyanates with  $\alpha,\alpha$ -dimethyl-3,5-dimethoxybenzyl alcohol in the presence of a suitable catalyst. For example, Scheme 1 shows the preparation of the Ddz derivative **1** of 1,6-diaminohexane. A slightly different route, available [6] for use with secondary amines.



SCHEME 1.

The photogeneration of free amines from their Ddz carbamates was studied both in solution and in the solid-state. In both cases the photocleavage proceeds with liberation of the free amine, carbon dioxide and 3,5-dimethoxy- $\alpha$ -methyl styrene as shown in Scheme 2 for the photo-precursor of 1,6-hexanediamine. Though alternate mechanistic pathways are possible, it is believed that the photocleavage proceeds by initial heterolytic cleavage of the benzylic C-O bond of the Ddz carbamate.



SCHEME 2.

This is facilitated by the strong electron donating effect of the methoxy substituents in the photochemically excited state. The solid state reaction was explored by monitoring the behavior of the photoactive carbamates within poly(methyl methacrylate) and poly(methacrylonitrile) matrices. Quantum yield measurements performed on such films spin-coated on quartz (UV measurements for PMMA films) and on NaCl windows (IR measurements for PMAN films) showed that the desired photocleavage and production of free amine occurred with a reasonably high efficiency as a value of 0.10 was obtained for the quantum yield in the solid-state

reaction. Figure 1 shows the change in carbonyl absorption of the  $\alpha,\alpha$ -dimethyl-3,5-dimethoxybenzyl carbamoylcyclohexane versus time upon UV exposure at 280nm.

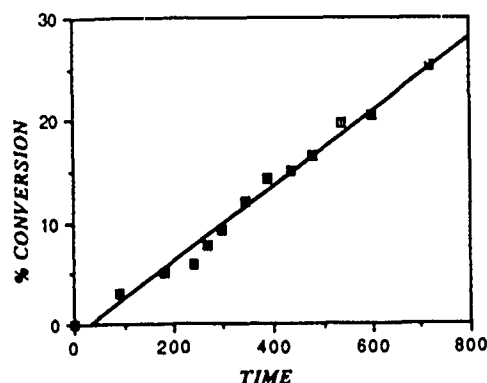


FIGURE 1.

Figure 2 shows a plot of log quantum yield versus number of quanta absorbed for the same  $\alpha,\alpha$ -dimethyl-3,5-dimethoxybenzyl carbamoylcyclohexane upon exposure at 280nm; as shown on this plot, extrapolation to zero results in a quantum yield value of 0.10 for this system.

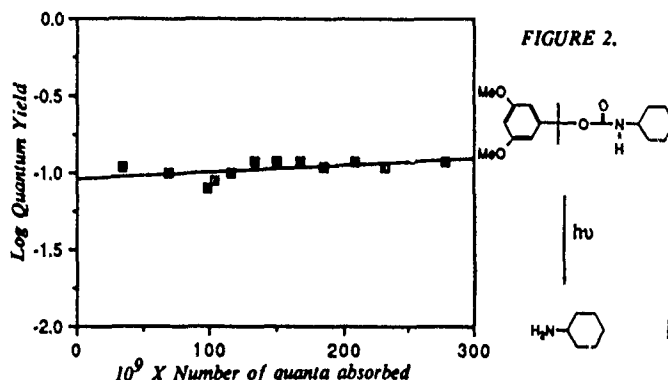
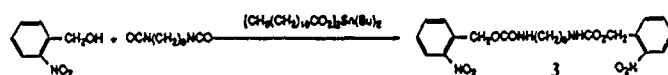


FIGURE 2.

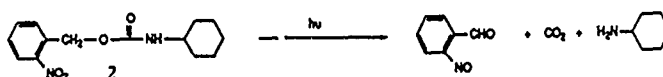
## 2 Chemistry of *o*-nitrobenzyl and analogous carbamates.

The photolabile 2-nitrobenzyl group has been used previously as a protecting group for alcohols, amino acids, and peptides. While earlier procedures have involved the use of 2-nitrobenzyl chloroformate in the protection step, and indeed we have used this reagent to prepare **2**, we have found that it is unsuitable for the protection of diamines such as hexane-1,6-diamine as decarboxylation occurs and the product that is isolated is the tertiary amine. In contrast, the direct addition of an alcohol to an isocyanate (Scheme 3) catalyzed by dibutyl tin dilaurate is very effective and can be used for example to prepare bis-carbamate **3**.



SCHEME 3.

Both **2** and **3** are photoactive and liberate cyclohexylamine and hexane-1,6-diamine respectively upon exposure to UV light below 400nm as shown in Scheme 4.

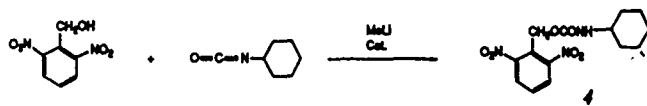


SCHEME 4.

The solid-state quantum efficiency of **2** can be determined by coating NaCl plates with a film of poly(methyl methacrylate) containing 7-10 mole % of **2** and monitoring the disappearance of the asymmetric N-O

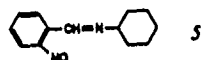
stretch by IR spectroscopy with increasing UV exposure dose. The deprotection reaction can easily be carried to completion but typical quantum yield measurements are best performed at conversions between 5 and 25%. Typical quantum efficiencies for the photodecomposition of **2** with liberation of cyclohexylamine are of the order of 0.13 at 254nm, a value which was calibrated by parallel solid-state measurements with the known [7] actinometer, 2-nitrobenzaldehyde.

In an attempt to increase this quantum yield, the 2,6-dinitrobenzyl group was substituted for the 2-nitrobenzyl group in the preparation of photoactive carbamate **4**. The best procedure for the preparation of **4** involved the reaction of 2,6-dinitrobenzyl alcohol with cyclohexyl isocyanate in the presence of a catalytic amount of methyl lithium. Carbamate **4** obtained in 78% yield was found to be remarkably active when irradiated with UV light below 400nm. For example its solid-state quantum efficiency at 254nm is 0.62 when exposed within a film of poly(methyl methacrylate) [8].

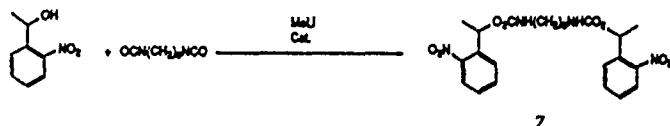
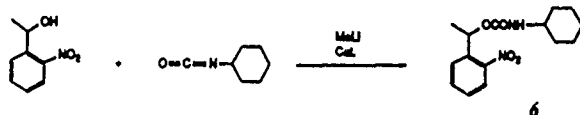


Earlier work on the use of similar 2-nitrobenzyl-based protecting groups in amino-acid chemistry had suggested that significant recombination of the liberated nitro-benzaldehyde with the newly freed amino-groups of the deprotected amino-acid was taking place [9]. This process, if prevalent, could be troublesome even though the resulting N-alkylimines would readily hydrolyze to free amines in the presence of water.

In an attempt to determine whether or not this process was significant with carbamates such as **2-4**, their photodecomposition in solution was monitored by GC-MS. These studies failed to show the presence of an imine such as **5** while free cyclohexylamine was observed and remained in solution even upon prolonged standing in the presence of other photo-products.



Nevertheless a third type of carbamate in which the photo by-product would be a nitroso ketone rather than a nitrosoaldehyde was also investigated as this by-product would be even less prone to spontaneous recombination with the liberated amine. Carbamate **6** was obtained in 71% yield by the lithium alkoxide catalyzed reaction of cyclohexyl isocyanate with  $\alpha$ -methyl-2-nitro benzenemethanol. Similarly, bis-carbamate **7** was obtained in 69% yield by the same reaction with 1,6-diisocyanatohexane.



Solid-state photolysis of **6** in a poly(methyl methacrylate) matrix showed a quantum efficiency of 0.11, while GC-MS monitoring of its photolysis in solution showed no evidence of imine formation while free cyclohexylamine was observed together with other photo-by-products.

The photoactive carbamates described in this study appear to be efficient photo precursors of free amines [6, 8]. The very high quantum efficiency obtained in the photolysis of **4** is of particular interest. Additional experiments involving the photocuring of epoxy resins with diamines liberated from **3** or **7** have further confirmed the usefulness of this new family of amine photo-precursors. These experiments as well as other developments involving the use of our photogenerated amines will be described elsewhere.

#### Acknowledgements.

Financial support of the preliminary studies for this project under a gift from IBM Corporation (Materials and Processing Science Program) as well as continuing support by the Office of Naval Research are gratefully acknowledged.

#### References

- 1) J.V. Crivello, J.H.W. Lam, *Macromolecules*, **10** (1977) 1307; J.V. Crivello, *Adv. Polym. Sci.*, **62** (1984) 1; J.V. Crivello, *Polym. Mat. Sci. Eng.*, **61** (1989) 62.
- 2) A. Reiser, "Photoreactive Polymers" Wiley-Interscience, 1989.
- 3) C.G. Willson, H. Ito, J.M.J. Fréchet, T.G. Tessier, F.M. Houlihan, *J. Electrochem. Soc.*, **133** (1986) 181.
- 4) J.M.J. Fréchet, F. Bouchard, E. Eichler, F.M. Houlihan, T. Iizawa, B. Kryczka, C.G. Willson, *Polymer Journal*, **19** (1987) 31; J.M.J. Fréchet, E. Eichler, M. Stanculescu, T. Iizawa, F. Bouchard, F.M. Houlihan, C.G. Willson, ACS Symposium Series, #346, "Polymers for High Technology in Electronics and Photonics" (1987) 138. J.M.J. Fréchet, C.G. Willson, T. Iizawa, T. Nishikubo, K. Igarashi, J. Fahey, ACS Symposium Series # 412 "Polymers in Microlithography", 1989, 100.
- 5) J.M.J. Fréchet, S. Matusczak, H.D.H. Stover, C.G. Willson, B. Reck, ACS Symposium Series # 412 "Polymers in Microlithography", 1989, 74.
- 6) J. F. Cameron, J.M.J. Fréchet, *J. Org. Chem.*, 1990, 0000 in press.
- 7) J.N. Pitts, K.S. Wan, E.A. Schuck, *J. Am. Chem. Soc.*, 1984, 86, 3606. *Ibid.*, 1968, 90, 1106.
- 8) J. F. Cameron, J.M.J. Fréchet, Submitted for publication.
- 9) A. Patchornik, B. Amit, R. B. Woodward, *J. Am. Chem. Soc.* 1970, 92, 6333.